

Chem 41c Final Exam

Stoltz, Spring 2007, June 4, 2007

The exam begins when you turn to page 2. You have 4 hours to complete the exam. This is a closed note and closed book exam with no collaboration. You may use the periodic table on the last page of this packet. You may not use any other materials. The exam has a total of 200 points and counts for 40% of your course grade. Good luck.

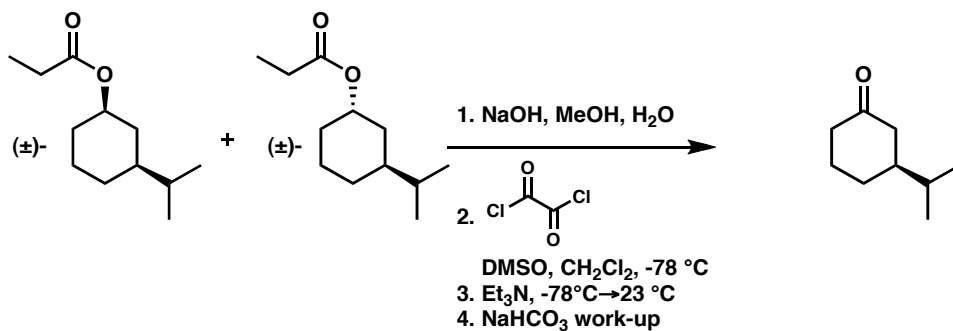
There are 16 pages in this exam packet.

The Exam is due by Friday June 8, 2006 by 5 PM.

Name: _____

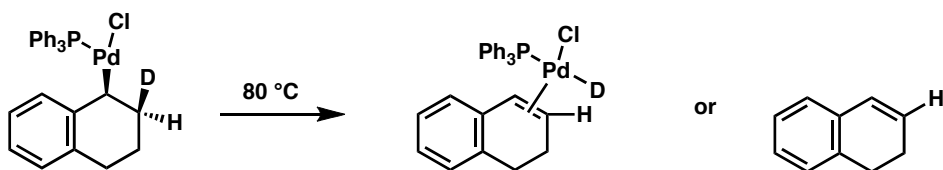
1. Predict the major non-volatile products (if any) of the following reactions or sequences. Clearly mark your answers by placing a **box** around the compound that you believe to be the major product. (5 points each).

a.

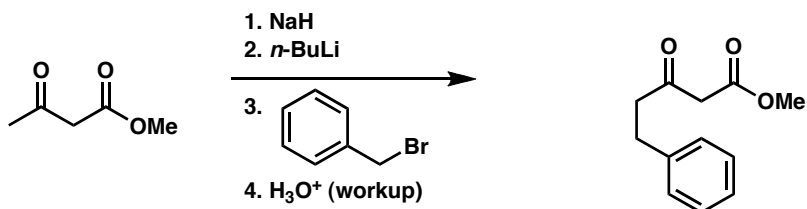


hint: one racemic non volatile product is formed

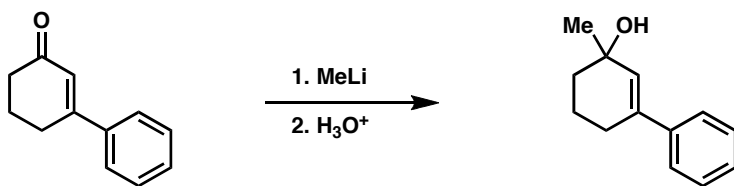
b.



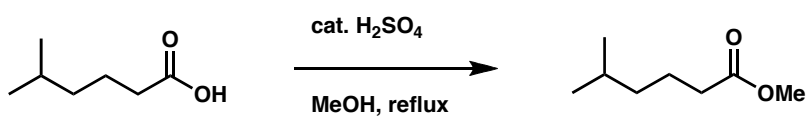
c.



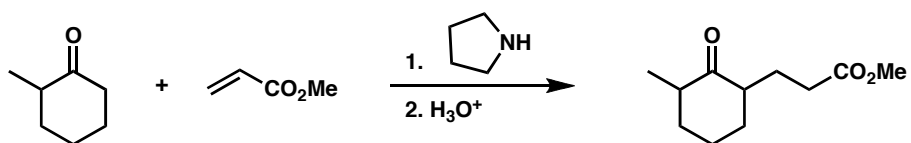
d.



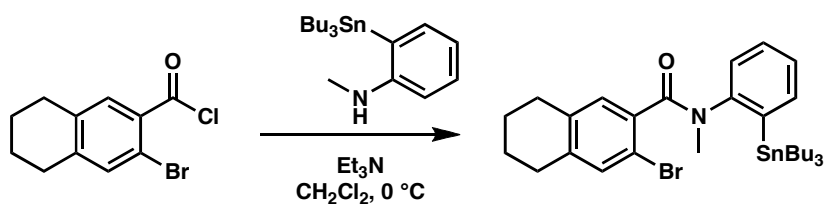
e.



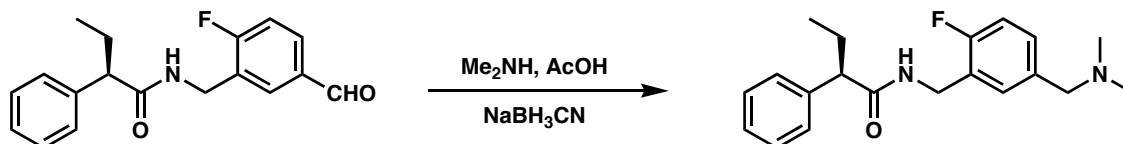
f.



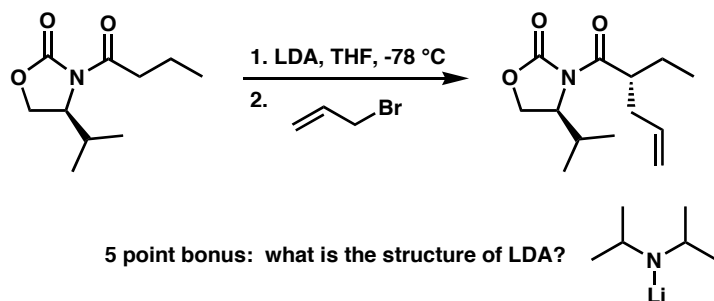
g.



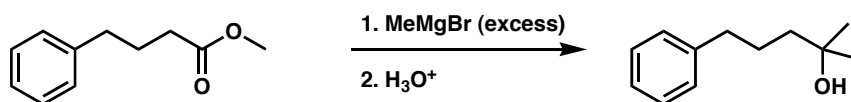
h.



i.

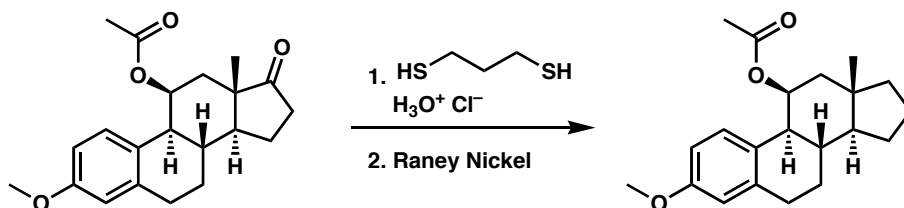


j.



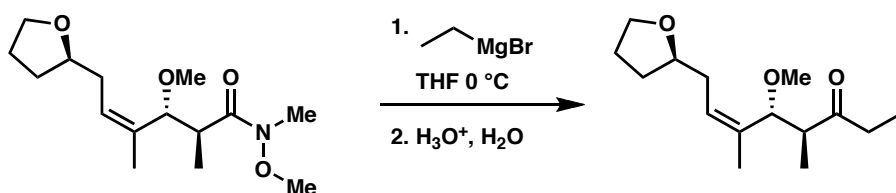
2. Provide reagents for the following transformations. They may be multistep processes, but should not be longer than 5 steps. (5 points each)

a.

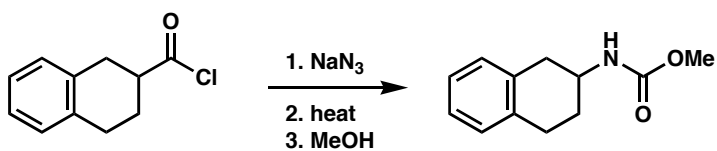


(maybe Clemmenson...not Wolf Kischner)

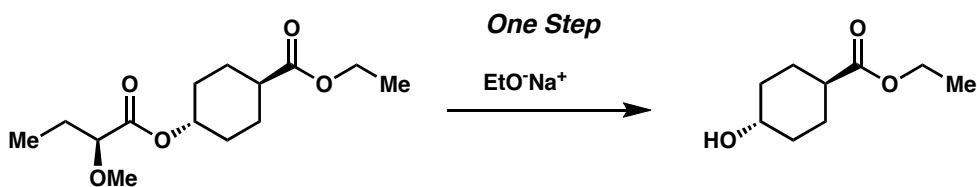
b.



c.

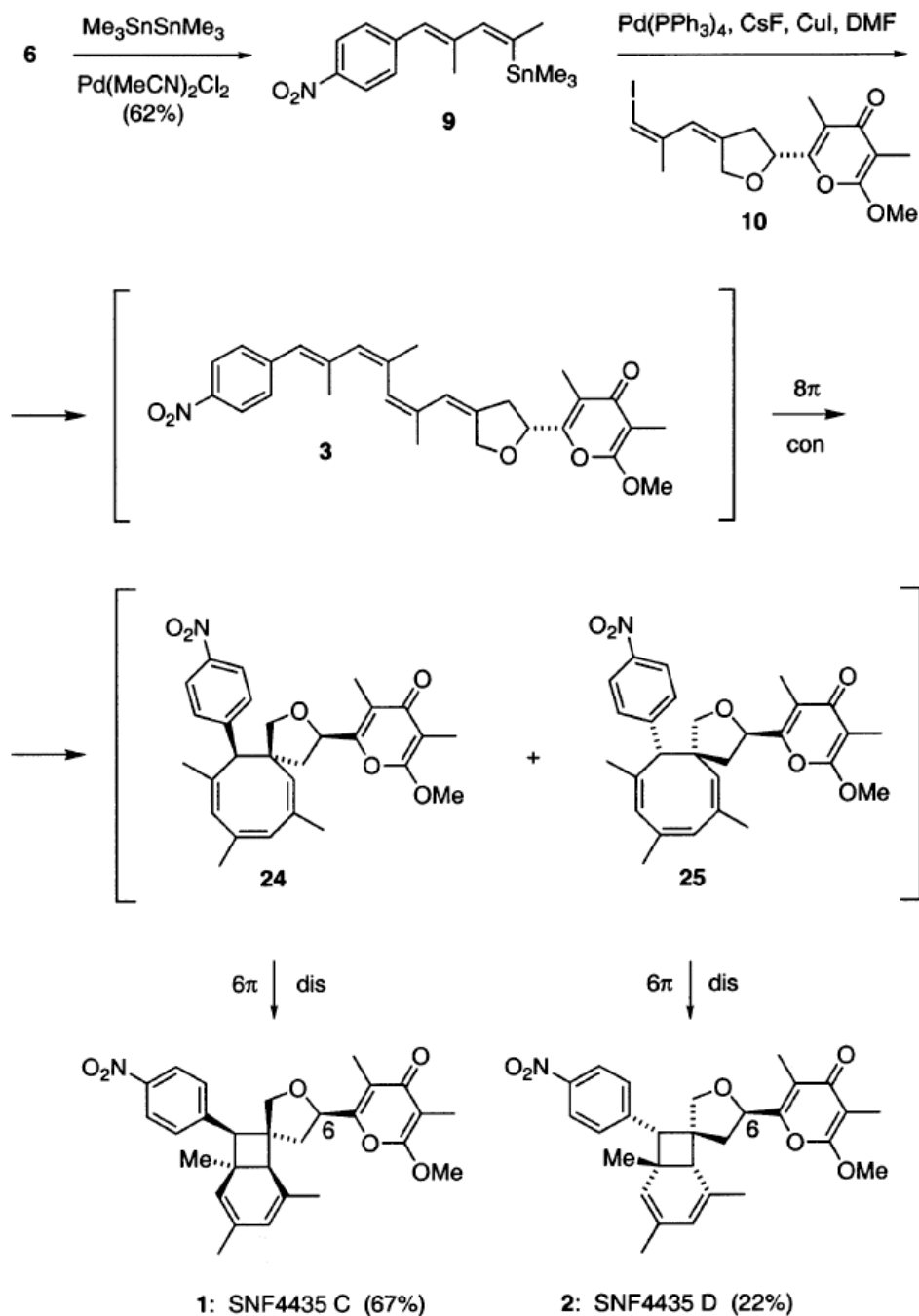


d.

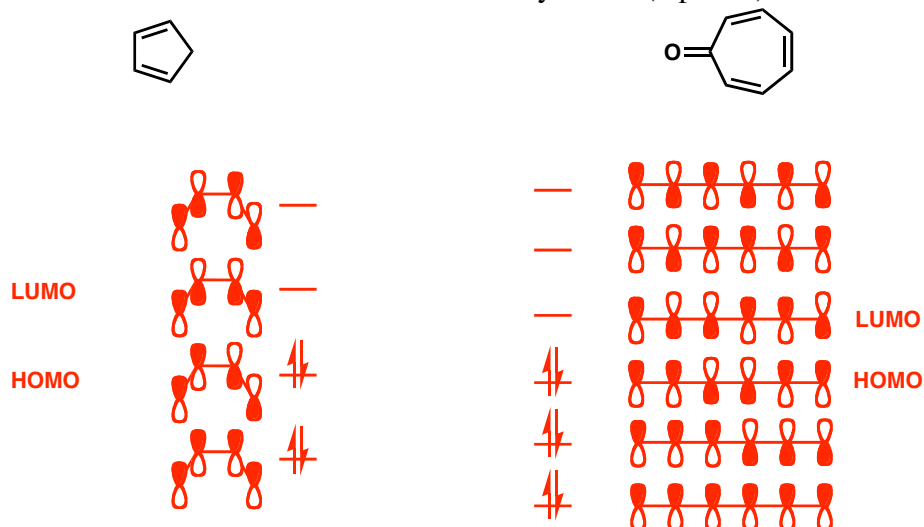


3. We have learned about transition metal-catalyzed processes and pericyclic reactions this term. A remarkable cascade of such reactions was recently reported to produce the unusual and interesting natural products SNF4435 C and D (compounds **1** and **2**). Scheme 5 is taken directly from the paper that describes their synthesis. Given your knowledge of these reactions, 1) predict the structure of intermediates **3**, **24**, and **25** 2) Describe a mechanism for the conversion of **3** to **24** and **25**, and from **24** and **25** to **1** and **2** (hint: it may be useful to draw an orbital diagram for **3** although not necessary) and 3) As a bonus provide a possible structure for **6**. (20 points, 10 point bonus)

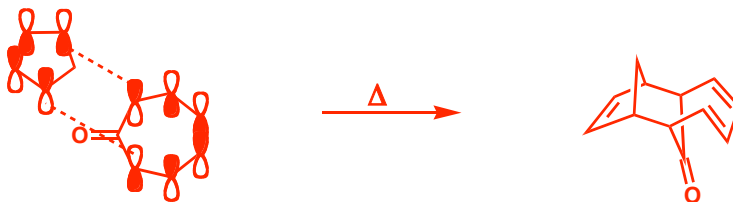
Scheme 5



4. a) Draw the molecular orbitals for the olefin-containing portions of the following conjugated systems. Fill in the electrons and label the HOMO and LUMO for each system.. (5 points)

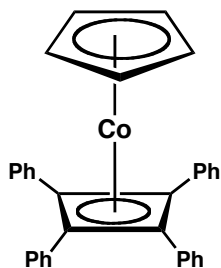


b) Predict the product of the thermal [6+4] cycloaddition of these two compounds. Is the process allowed by frontier molecular orbital theory? Hint: Draw the compounds with the appropriate molecular orbitals first. (5 points)



5. In the following complexes, what is the formal oxidation state of the metal, the d^n description, and the electron count? Feel free to use the periodic table in the room (5 points each-no partial credit)

a.

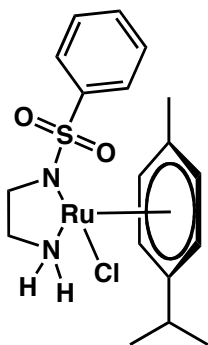


Co(I)
or
Co¹⁺

d^8

18 electron complex

b.

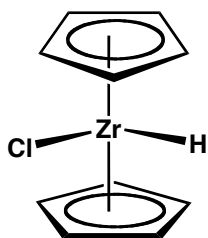


Ru(II)
or
Ru²⁺

d^6

18 electron complex

c.

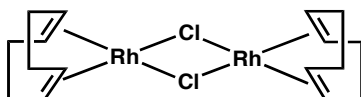


Zr(IV)
or
Zr⁴⁺

d^0

16 electron complex

d.

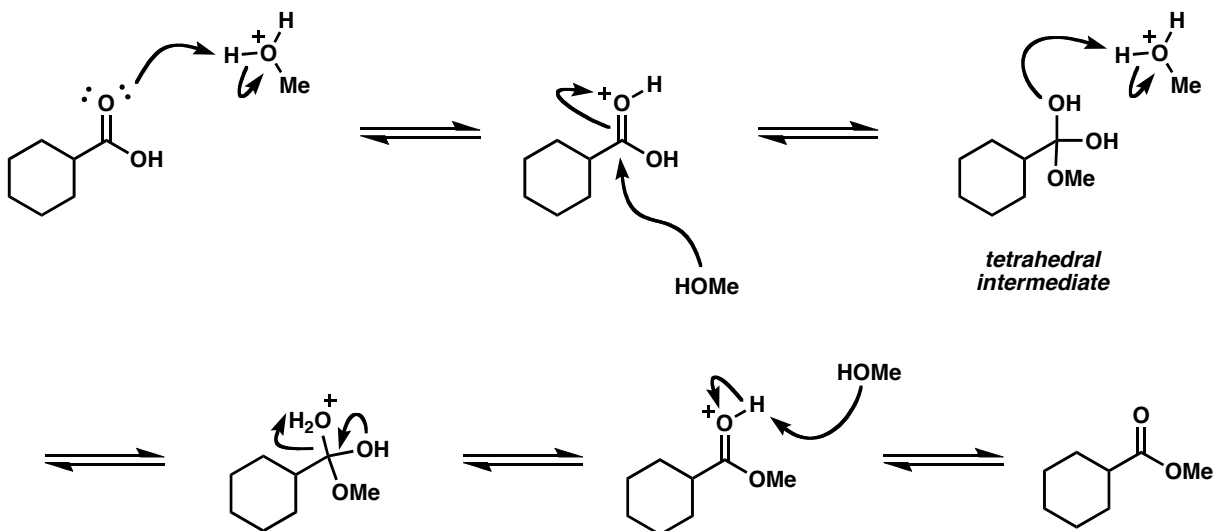
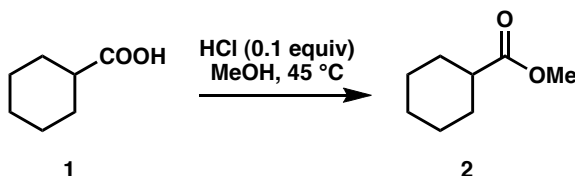


Rh(I)
or
Rh⁺¹

d^8

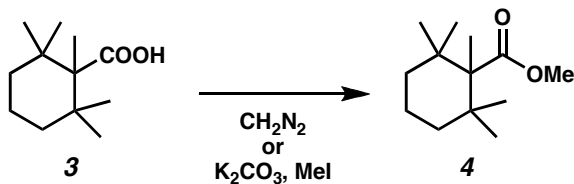
16 electron each Rh

6. a) Provide a detailed curved arrow mechanism for the following reaction. What drives the equilibrium to the product side? (10 points)

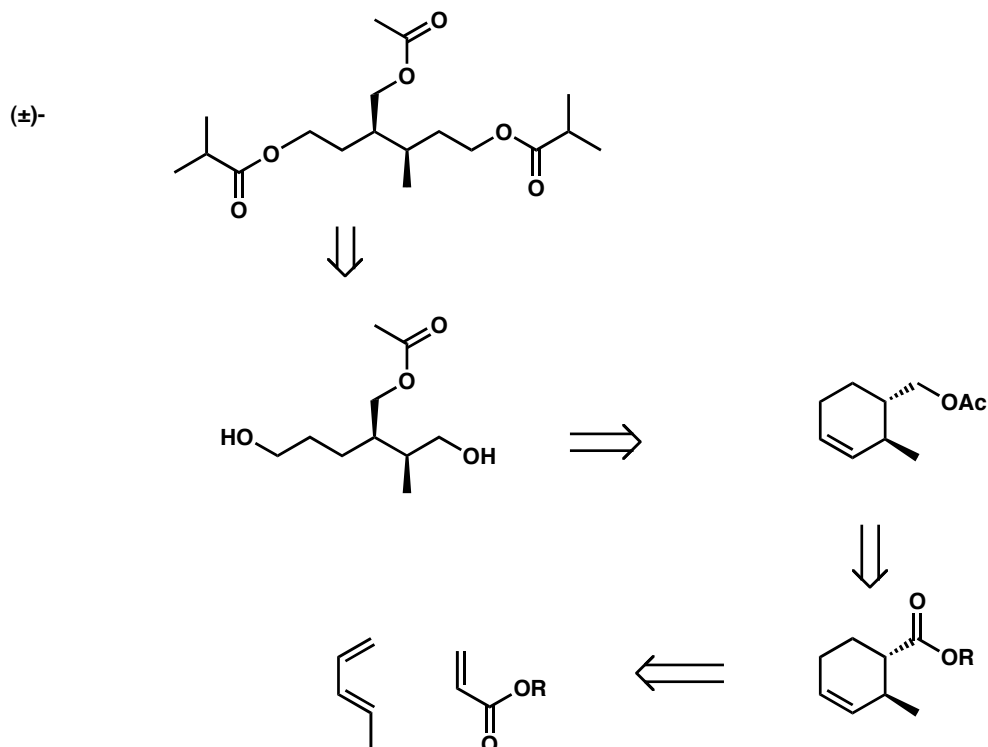


Reaction driven to completion due to large excess of alcohol (MeOH).

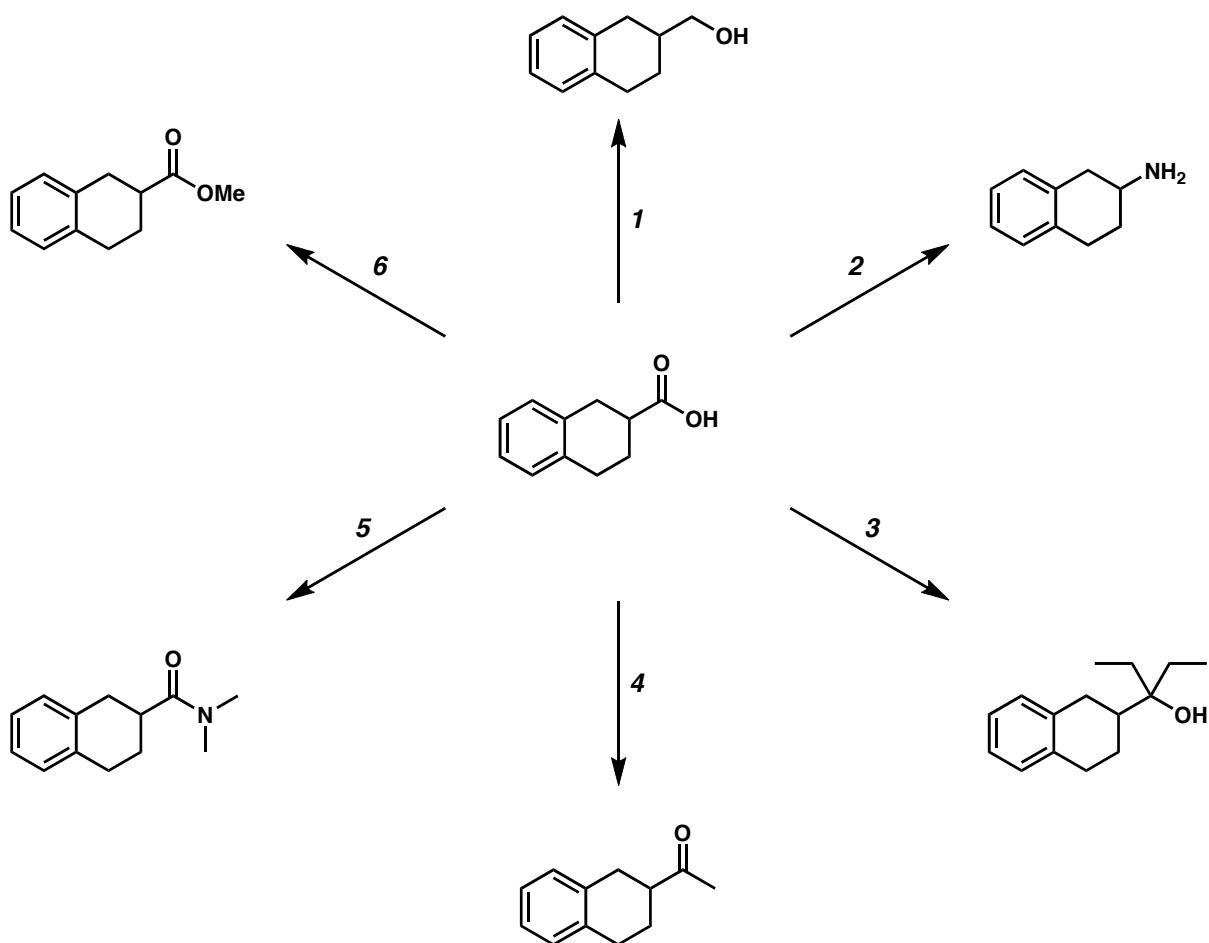
b) In contrast to part a of this problem, under the same conditions the following reaction (**3**→**4**) is extremely slow. Why do you think this is the case? Provide an alternative method for preparing the methyl ester **4** from carboxylic acid **3** that you believe would be fast and high yielding. Provide a detailed curved arrow mechanism for your new synthesis of **4** from **3** and explain why the new method should be better. (10 points)



7. Imagine yourself in graduate school (let's say in 2011)...On a late summer afternoon, a good Bostonian friend of yours from the lab presents you with the opportunity to see the first place Red Sox play the bottom feeder New York Yankees at Fenway Park the following afternoon. Since you are in California, you will need to catch the red-eye that night in order to make the first pitch the next day. You are in desperate need of bulletproof route to your target molecule (**1**), so that your SURF student will have something to do besides playing video games and washing dishes. Design a retrosynthesis of **1** and outline a complete forward synthesis for the following compound as a single diastereomer (in racemic form) starting from fragments of less than 6 carbons (or benzene). Just think, if you complete your task on time, you will not only get to witness four-time Cy Young award winner Daisuke Matsuzaka pitch for the perennial World Champion Boston Red Sox, but your SURF student will complete your project by the time you get back to Cali! (20 points)



8. As you can see, carboxylic acids are valuable synthons in organic chemistry. Provide reagents for each of the following six transformations in the spaces below the figure. Keep in mind that some transformations may require more than one step. (20 points)



1. LiAlH₄

2. 1. SOCl₂
2. NaN₃, then Δ
3. H₂O

3. 1. CH₂N₂
2. EtMgBr (excess)

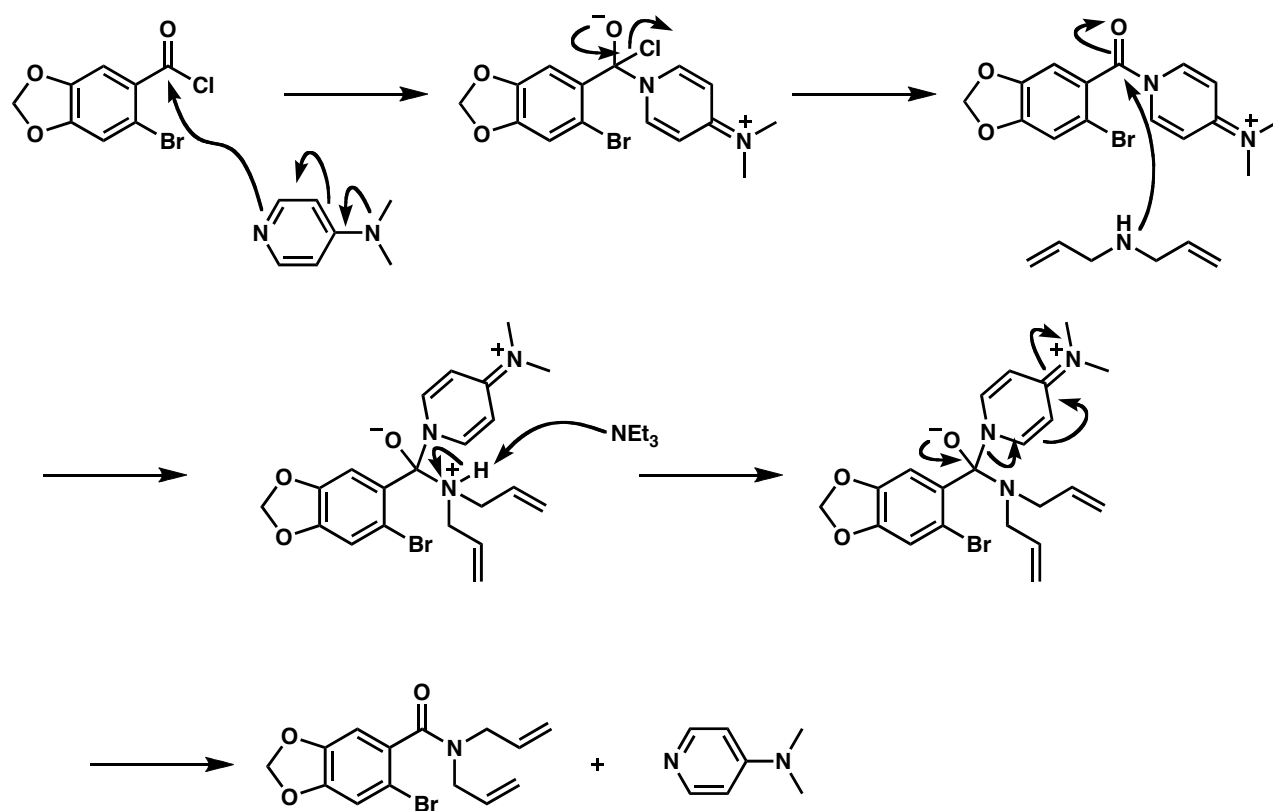
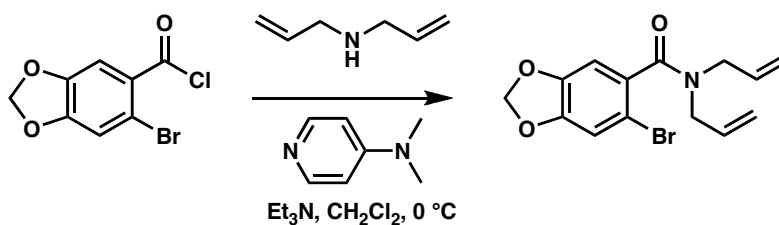
4. 1. SOCl₂
2. HN(OMe)Me
3. MeMgBr

5. 1. SOCl₂
2. Me₂NH

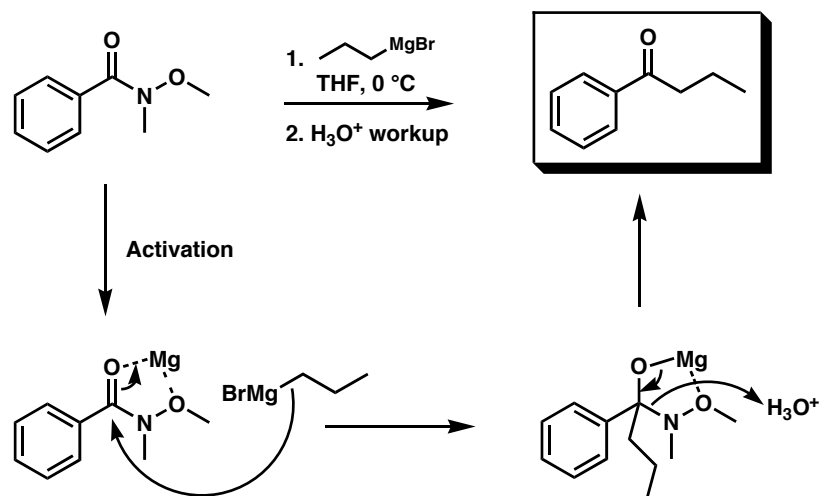
6. MeOH, H⁺ or CH₂N₂

9. Predict the product of these reactions and provide curved arrow mechanisms for each. (20 points)

a.



b.



PERIODIC TABLE OF THE ELEMENTS
<http://www.ktf-split.hr/periodni/en/>

GROUP NUMBERS IUPAC RECOMMENDATION (1985) GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)

ATOMIC NUMBER RELATIVE ATOMIC MASS (1)

SYMBOL ELEMENT NAME

1	IA	1	1.0079	1	H	1	1.0079	18	VIIIA	2	4.0026	18	He
1	IA	1	1.0079	1	H	1	1.0079	18	VIIIA	2	4.0026	18	He
2	IIA	2	9.0122	2	Be	2	9.0122	10	Ne	10	20.180	10	Ne
3	IIIA	3	6.941	3	Li	3	6.941	13	B	13	10.811	13	B
4	IIIA	4	9.0122	4	Be	4	9.0122	14	C	14	12.011	14	C
5	IIIA	5	10.811	5	B	5	10.811	15	N	15	14.007	15	N
6	IIIA	6	12.011	6	C	6	12.011	16	O	16	15.999	16	O
7	IIIA	7	14.007	7	N	7	14.007	17	F	17	18.998	17	F
8	IIIA	8	15.999	8	O	8	15.999	18	Ne	18	20.180	18	Ne
9	IIIA	9	18.998	9	F	9	18.998	19	K	19	39.098	19	K
10	IIIA	10	20.180	10	Ne	10	20.180	20	Ca	20	40.078	20	Ca
11	IIIA	11	22.990	11	Na	11	22.990	21	Sc	21	44.956	21	Sc
12	IIIA	12	24.305	12	Mg	12	24.305	22	Ti	22	47.867	22	Ti
13	IIIA	13	26.982	13	Al	13	26.982	23	V	23	50.942	23	V
14	IIIA	14	28.086	14	Si	14	28.086	24	Cr	24	51.996	24	Cr
15	IIIA	15	30.974	15	P	15	30.974	25	Mn	25	54.938	25	Mn
16	IIIA	16	32.065	16	S	16	32.065	26	Fe	26	55.845	26	Fe
17	IIIA	17	35.453	17	Cl	17	35.453	27	Co	27	58.933	27	Co
18	IIIA	18	39.948	18	Ar	18	39.948	28	Ni	28	58.693	28	Ni
19	IIIA	19	39.098	19	K	19	39.098	29	Cu	29	63.546	29	Cu
20	IIIA	20	40.078	20	Ca	20	40.078	30	Zn	30	65.39	30	Zn
21	IIIA	21	44.956	21	Sc	21	44.956	31	Ga	31	69.723	31	Ga
22	IIIA	22	47.867	22	Ti	22	47.867	32	Ge	32	72.64	32	Ge
23	IIIA	23	50.942	23	V	23	50.942	33	As	33	74.922	33	As
24	IIIA	24	51.996	24	Cr	24	51.996	34	Se	34	78.96	34	Se
25	IIIA	25	54.938	25	Mn	25	54.938	35	Br	35	79.904	35	Br
26	IIIA	26	55.845	26	Fe	26	55.845	36	Kr	36	83.80	36	Kr
27	IIIA	27	58.933	27	Co	27	58.933	37	Rb	37	85.468	37	Rb
28	IIIA	28	58.693	28	Ni	28	58.693	38	Sr	38	87.62	38	Sr
29	IIIA	29	63.546	29	Cu	29	63.546	39	Y	39	88.906	39	Y
30	IIIA	30	65.39	30	Zn	30	65.39	40	Zr	40	91.224	40	Zr
31	IIIA	31	69.723	31	Ga	31	69.723	41	Nb	41	92.906	41	Nb
32	IIIA	32	72.64	32	Ge	32	72.64	42	Mo	42	95.94	42	Mo
33	IIIA	33	74.922	33	As	33	74.922	43	Tc	43	(98)	43	Tc
34	IIIA	34	78.96	34	Se	34	78.96	44	Ru	44	101.07	44	Ru
35	IIIA	35	79.904	35	Br	35	79.904	45	Rh	45	102.91	45	Rh
36	IIIA	36	83.80	36	Kr	36	83.80	46	Pd	46	106.42	46	Pd
37	IIIA	37	85.468	37	Rb	37	85.468	47	Ag	47	107.87	47	Ag
38	IIIA	38	87.62	38	Sr	38	87.62	48	Cd	48	112.41	48	Cd
39	IIIA	39	88.906	39	Y	39	88.906	49	In	49	114.82	49	In
40	IIIA	40	91.224	40	Zr	40	91.224	50	Sn	50	118.71	50	Sn
41	IIIA	41	92.906	41	Nb	41	92.906	51	Sb	51	121.76	51	Sb
42	IIIA	42	95.94	42	Mo	42	95.94	52	Te	52	127.60	52	Te
43	IIIA	43	(98)	43	Tc	43	(98)	53	I	53	126.90	53	I
44	IIIA	44	101.07	44	Ru	44	101.07	54	Xe	54	131.29	54	Xe
45	IIIA	45	102.91	45	Rh	45	102.91	55	Cs	55	132.91	55	Cs
46	IIIA	46	106.42	46	Pd	46	106.42	56	Ba	56	137.33	56	Ba
47	IIIA	47	107.87	47	Ag	47	107.87	57	La-Lu	57	71	57	La-Lu
48	IIIA	48	112.41	48	Cd	48	112.41	58	Hf	58	178.49	58	Hf
49	IIIA	49	114.82	49	In	49	114.82	59	Ta	59	180.95	59	Ta
50	IIIA	50	118.71	50	Sn	50	118.71	60	W	60	183.84	60	W
51	IIIA	51	121.76	51	Sb	51	121.76	61	Re	61	186.21	61	Re
52	IIIA	52	127.60	52	Te	52	127.60	62	Os	62	190.23	62	Os
53	IIIA	53	126.90	53	I	53	126.90	63	Ir	63	192.22	63	Ir
54	IIIA	54	131.29	54	Xe	54	131.29	64	Pt	64	195.08	64	Pt
55	IIIA	55	132.91	55	Cs	55	132.91	65	Au	65	196.97	65	Au
56	IIIA	56	137.33	56	Ba	56	137.33	66	Hg	66	200.59	66	Hg
57	IIIA	57	71	57	La-Lu	57	71	67	Tl	67	204.38	67	Tl
58	IIIA	58	178.49	58	Hf	58	178.49	68	Pb	68	207.2	68	Pb
59	IIIA	59	180.95	59	Ta	59	180.95	69	Bi	69	208.98	69	Bi
60	IIIA	60	183.84	60	W	60	183.84	70	Po	70	(209)	70	Po
61	IIIA	61	186.21	61	Re	61	186.21	71	At	71	(210)	71	At
62	IIIA	62	190.23	62	Os	62	190.23	72	Rn	72	(222)	72	Rn
63	IIIA	63	192.22	63	Ir	63	192.22	73	Fr	73	(223)	73	Fr
64	IIIA	64	195.08	64	Pt	64	195.08	74	Ra	74	(226)	74	Ra
65	IIIA	65	196.97	65	Au	65	196.97	75	Ac-Lr	75	103	75	Ac-Lr
66	IIIA	66	200.59	66	Hg	66	200.59	76	Rf	76	(261)	76	Rf
67	IIIA	67	204.38	67	Tl	67	204.38	77	Db	77	(262)	77	Db
68	IIIA	68	207.2	68	Pb	68	207.2	78	Sg	78	(266)	78	Sg
69	IIIA	69	208.98	69	Bi	69	208.98	79	Bh	79	(264)	79	Bh
70	IIIA	70	(209)	70	Po	70	(209)	80	Hs	80	(277)	80	Hs
71	IIIA	71	(210)	71	At	71	(210)	81	Mt	81	(268)	81	Mt
72	IIIA	72	(222)	72	Rn	72	(222)	82	Uun	82	(281)	82	Uun
73	IIIA	73	(223)	73	Fr	73	(223)	83	Uuu	83	(272)	83	Uuu
74	IIIA	74	(226)	74	Ra	74	(226)	84	Uub	84	(285)	84	Uub
75	IIIA	75	103	75	Ac-Lr	75	103	85	Uuq	85	(289)	85	Uuq
76	IIIA	76	178.49	76	Hf	76	178.49	86	Uup	86	(293)	86	Uup
77	IIIA	77	180.95	77	Ta	77	180.95	87	Uuh	87	(297)	87	Uuh
78	IIIA	78	183.84	78	W	78	183.84	88	Uuq	88	(293)	88	Uuq
79	IIIA	79	186.21	79	Re	79	186.21	89	Uuo	89	(304)	89	Uuo
80	IIIA	80	190.23	80	Os	80	190.23	90	Uuq	90	(310)	90	Uuq
81	IIIA	81	192.22	81	Ir	81	192.22	91	Uuq	91	(315)	91	Uuq
82	IIIA	82	195.08	82	Pt	82	195.08	92	Uuq	92	(318)	92	Uuq
83	IIIA	83	196.97	83	Au	83	196.97	93	Uuq	93	(321)	93	Uuq
84	IIIA	84	200.59	84	Hg	84	200.59	94	Uuq	94	(324)	94	Uuq
85	IIIA	85	204.38	85	Tl	85	204.38	95	Uuq	95	(327)	95	Uuq
86	IIIA	86	207.2	86	Pb	86	207.2	96	Uuq	96	(330)	96	Uuq
87	IIIA	87	208.98	87	Bi	87	208.98	97	Uuq	97	(332)	97	Uuq
88	IIIA	88	(209)	88	Po	88	(209)	98	Uuq	98	(335)	98	Uuq
89	IIIA	89	(210)	89	At	89	(210)	99	Uuq	99	(338)	99	Uuq
90	IIIA	90	(222)	90	Rn	90	(222)	100	Uuq	100	(341)	100	Uuq
91	IIIA	91	(223)	91	Fr	91	(223)	101	Uuq	101	(344)	101	Uuq
92	IIIA	92	(226)	92	Ra	92	(226)	102	Uuq	102	(347)	102	Uuq
93	IIIA	93	103	93	Ac-Lr	93	103	103	Uuq	103	(350)	103	Uuq
94	IIIA	94	178.49	94	Hf	94	178.49	104	Uuq	104	(353)	104	Uuq
95	IIIA	95	180.95	95	Ta	95	180.95	105	Uuq	105	(356)	105	Uuq
96	IIIA	96	183.84	96	W	96	183.84	106	Uuq	106	(359)	106	Uuq
97	IIIA	97	186.21	97	Re	97	186.21	107	Uuq	107	(362)	107	Uuq
98	IIIA	98	190.23	98	Os	98	190.23	108	Uuq	108	(365)	108	Uuq
99	IIIA	99	192.22	99	Ir	99	192.22	109	Uuq	109	(368)	109	Uuq
100	IIIA	100	195.08	100	Pt	100	195.08	110	Uuq	110	(371)	110	Uuq
101	IIIA	101	196.97	101	Au	101	196.97	111	Uuq	111	(374)	111	Uuq
102	IIIA	102	200.59	102	Hg	102	200.59	112	Uuq	112	(377)	112	Uuq
103	IIIA	103	204.38	103	Tl	103	204.38	113	Uuq	113	(381)	113	Uuq
104	IIIA	104	207.2	104	Pb	104	207.2	114	Uuq	114	(384)	114	Uuq
105	IIIA	105	208.98	105	Bi	105	208.98	115	Uuq	115	(387)	115	Uuq
106	IIIA	106	(209)	106	Po	106	(209)	116	Uuq	116	(390		